free energies appear in the last column of the table. The differences between these results and those which were given in the preceding papers vary from 100 cal. in the cases of mannitol and glucose to 5000 cal. for palmitic acid. The accuracy of these revised values is now almost entirely limited by the accuracy of the heats of combustion involved.

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THE KINETICS OF THE OXIDATION OF IODIDE ION BY ACID DICHROMATE SOLUTIONS IN PRESENCE OF A NEUTRAL SALT

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Introduction

Many ionic reactions show kinetic anomalies in the sense that the order of reaction does not come out an integral number. Brönsted[2] has made the suggestion that if sufficient neutral salt be added to fix the activity coefficients of the ions, such reactions can be rendered normal.

The oxidation of iodide ion by means of potassium dichromate in acid solution is a reaction of this type.

DeLury[3] and also Kernot and Pietrofesa[4] concluded from their work that the reaction was first order with respect to $Cr_2O_7^{--}$ ion, nearly second order with respect to H^+ ion and between first and second with respect to I^- ion. In the preliminary work of this investigation the data confirmed the results of the above-named workers, but the order of reaction with respect to I^- ion was found to be more nearly second than first. Thus the reaction considered as a whole appeared to be approximately a fifth order one.

The purpose of this work is to test Brönsted's prediction regarding the effect of neutral salt on the kinetics of the reaction and, if possible, to obtain experimental evidence bearing on the activity rate theory of reaction mechanism.

Outline of Experimental Work

A preliminary investigation was made over a wide range of salt concentration. The salt used was sodium chloride and the source of H^+ ion was perchloric acid. Sixteen reaction mixtures were made up with the concen-

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[1] Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Minnesota, June, 1928.

[2] Brönsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, New York, **1927**, p. 13.

[3] DeLury, *J. Phys. Chem.*, **7**, 239 (1903).

[4] Kernot and Pietrofesa, *Rend. accad. sci. fis. mat. Napoli*, **IIIA**, 275 (1911).

tration of sodium chloride as shown in Table I. The intial concentrations of the reactants were the same in all determinations and were as follows: $K_2Cr_2O_7$, 2.02×10^{-4} *M;* KI, 142×10^{-4} *M;* $HClO_4$, 364×10^{-4} *M.*

The reaction time was twenty minutes in each case, the extent of reaction being determined by titration with *N*/100 sodium thiosulfate, using starch solution as the indicator. All the solutions except the potassium iodide were mixed in a 250-cc. Erlenmeyer flask. The iodide was placed in a similar flask, both flasks being placed in a constant-temperature bath at 25°. When the temperature of the bath had been assumed, the mixed solutions were poured rapidly into the flask containing the iodide solution and then immediately returned to the first flask, both flasks then being replaced in the water-bath. The total volume of the reaction mixture was 100 cc. At the end of the chosen time interval, 25 cc. of a solution containing 110 g. of sodium acetate and 10 g. of sodium bicarbonate per liter was added to stop the reaction. The titration with sodium thiosulfate was then immediately made. A 5-cc. buret graduated to 0.02 cc. was used in making all titrations.

Calculation of the Velocity Constant

Since the concentrations of acid and iodide were greatly in excess over the dichromate, the velocity of reaction could be assumed to be proportional solely to the concentration of the latter. Under these conditions the work of DeLury, and of Kernot and Pietrofesa, and also the results presented in this paper, indicate pretty clearly that the reaction is first order with respect to dichromate (note the constant values of *k* in Tables III and IV). As a basis for the calculation, the "infinity" value for the reaction was taken as the average of the last two thiosulfate readings shown in Table I, Col. 3. The experimental results are exhibited in Table I and Fig. 1.

Table I

Showing the Salt Effect on the First-Order Velocity Constant Due to Varying Concentrations of Sodium Chloride for Constant Time Intervals of Twenty Minutes

Initial H^+, 364×10^{-4} *M;* I^-, 142×10^{-4} *M;* $Cr_2O_7^{--}$, 2.02×10^{-4} *M.*

Expt.	C_{NaCl}, *M*	$Na_2S_2O_3$, 0.00986 *M*, cc.	2 + log *k*	$\sqrt{\mu}$ total
1	0.0	4.15	0.314	0.226
2	.01	3.93	.293	.247
3	.025	3.74	.259	.276
4	.10	3.22	.182	.388
5	.20	2.88	.126	.500
6	.40	2.68	.090	.671
7	.50	2.68	.090	.741
8	.60	2.82	.114	.806
9	.80	2.80	.112	.921
10	1.0	3.20	0.179	1.024
11	1.4	3.89	.279	1.204
12	1.8	4.86	.401	1.360
13	2.2	6.12	.537	1.500
14	2.6	7.61	.684	1.628
15	3.0	9.30	.849	1.746
16	4.0	12.29[a]	...	...
17	5.0	12.08[a]	...	...

[a] Reaction completed.

Discussion of Figure 1

In Fig. 1 the logarithm of the first-order velocity constant, *k*, is plotted against the square root of the ionic strength, $\sqrt{\mu}$. The rather surprising results obtained are difficult to interpret. In general, the curve in the figure is very similar to activity curves for strong acids when plotted as a function of $\sqrt{\mu}$. The minimum in the curve appears at an ionic strength of about 0.5, which is about the point at which the minimum occurs in activity curves for strong acids. Unfortunately, little is known concerning the variation of the activity of dichromate and hydriodic acid over this range of ionic strength. If data on this point were available it might be possible to interpret the minimum in the reaction velocity in more detail. However, in the light of Brönsted's theory it is possible to explain the results obtained in the more dilute solutions. For the detail of the Brönsted theory, the reader is referred to the original papers.[5] The following is a brief outline of some of the more essential features.

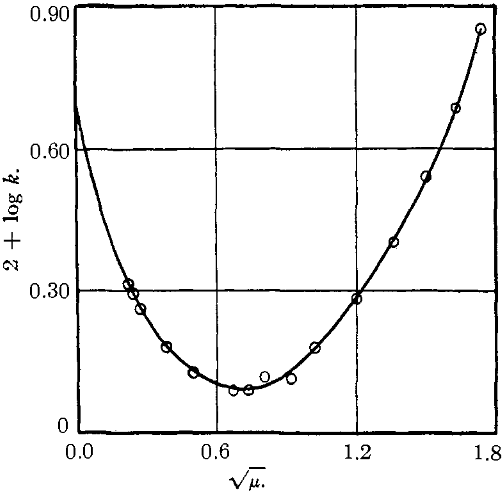

Fig. 1.—Curve showing the effect of neutral salt on the first-order constant, the initial concentrations of H^+, I^- and CrO_{27}^{--} being maintained constant throughout.

According to the classical theory, the expression for the velocity of reaction in the case of a trimolecular reaction may be written $h = k_1c_Ac_Bc_C$. The corresponding expression derived from the "activity theory" is $h = k_2a_Aa_Ba_C$. In these expressions c and a represent concentrations and activities, respectively. Brönsted drives the expression $h = kc_Ac_Bc_Cf_Af_Bf_C/f_x$ for a trimolecular reaction, where $f_Af_Bf_C$ and f_x denote the activity coefficients of A, B, C and x, respectively. x is a complex ion formed by the collision of A, B and C. Since in dilute solutions the activity coefficients of ions depend largely on the charges borne by the ions, and since the charge of x is the algebraic sum of the charges of A, B and C, the application of the Brönsted equation to the calculation of reaction velocities is made possible. Combining the Brönsted with the classical expression we obtain $k_1 = kf_Af_Bf_C/f_x$. For the calculation of the "kinetic activity

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[5] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); Brönsted, *ibid.*, **115**, 337 (1925); Brönsted and Delbanco, *Z. anorg. Chem.*, **144**, 248 (1925).

factor," $f_Af_Bf_C/f_x$, the Debye expression,[6] $-\log f = Az^2\sqrt{\mu}$, may be employed. In this last equation z is the valence of a particular ion, μ is the ionic strength and the factor A has a value of about 0.5 and is so taken for the calculation. Brönsted's development finally leads to the relation: $\log k_1 = \log k+(z_Az_B + z_Az_C + z_Bz_C)\sqrt{\mu}$ for a trimolecular reaction. If now $\log k_1$ as ordinate is plotted against $\sqrt{\mu}$ as abscissa, a straight line should result with a slope equal to $(z_Az_B + z_Az_C + z_Bz_C)$ and with an intercept $\log k$ on the ordinate axis. Considerable evidence[7] has been presented in support of this theory, but so far as the authors are aware no previous attempt has been made to apply the Brönsted theory to trimolecular or more complex reactions.

Assuming for the sake of argument that our reaction is trimolecular, we may let A, B and C be $Cr_2O_7^{--}$, H^+ and I^-, respectively. Thus $z_A = -2$, $z_B = 1$, $z_C = -1$. Substituting these values in the above equation, it becomes, $\log k_1 = \log k + (-1)\sqrt{\mu}$. A plot of $\log k_1$ *versus* $\sqrt{\mu}$ would have a slope of (-1) under these conditions.

On the other hand, if the reaction be pentamolecular, as the work of DeLury and others and many of the experimental results obtained in the preliminary work of this research seem to indicate, it can be shown that this would lead to the equation

$$\log k_1 = \log k + (z_Az_B + z_Az_C + z_Az_D + z_Az_E + z_Bz_C + z_Bz_D + z_Bz_E + z_Cz_D + z_Cz_E + z_Dz_E)$$

Letting A represent $Cr_2O_7^{--}$, and B and C represent H^+, and D and E, I^-, the expression simplifies to $\log k_1 = \log k + (-2)\sqrt{\mu}$.

Later on in this paper evidence will be given showing that the reaction really consists of two simultaneous reactions, one involving $Cr_2O_7^{--}$, H^+ and I^- to the first power and the other involving $Cr_2O_7^{--}$ to the first power and H^+ and I^- to the second power. Furthermore, calculations

TABLE II

EFFECT OF VERY LOW SODIUM CHLORIDE CONCENTRATION ON THE FIRST-ORDER VELOCITY CONSTANT FOR CONSTANT TIME INTERVALS OF TWENTY MINUTES

Initial H^+, 364×10^{-4} *M;* I^-, 142×10^{-4} *M;* $Cr_2O_7^{--}$, 2.02×10^{-4} M.

Expt.	C_{NaCl}	$Na_2S_2O_3$, cc.	$2 + \log k$	$\sqrt{\mu}$, total
1	0.00	3.74, 3.69, 3.84, 3.84 (av. 3.78)	0.271	0.226
2	.005	3.72, 3.70, 3.66, 3.72, 3.69 (av. 3.70)	.260	.237
3	.01	3.62, 3.60, 3.60, 3.66, 3.62 (av. 3.62)	.248	.247
4	.02	3.52, 3.50, 3.54, 3.49 (av. 3.51)	.232	.267
5	.03	3.34, 3.38, 3.30 (av. 3.34)	.210	.285
6	.04	3.27, 3.24, 3.31, 3.30 (av. 3.28)	.197	.302
7	.05	3.25, 3.22, 3.20, 3.20, 3.18 (av. 3.21)	.186	.318
8	.06	3.14, 3.15, 3.12, 3.16, 3.14 (av. 3.14)	.175	.333

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[6] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[7] Brönsted and Livingston, *ibid.*, **49**, 435 (1927); Livingston and Bray, *ibid.*, **45**, 2048 (1923); Brönsted and Delbanco, *Z. anorg. Chem.*, **144**, 248 (1925).

from the data show that about 65% of the transformation is brought about by the pentamolecular reaction. Consequently, if a plot of log k_1 against $\sqrt{\mu}$ be made, the slope of the resulting line should be -1.65 at low ionic strength. The data of Table II were thus plotted in Fig. 2. It will be seen that the experimental curve is asymptotically tangent to the theoretical slope -1.65. The magnitude of the ionic strength in these experiments is, of course, too great to expect that the points would actually fall on a line with the theoretical slope. Actual coincidence of such experimental curves with the theoretical is only obtained at ionic strengths $\sqrt{\mu} = 0.15$ or less (see work of Brönsted cited above). Unfortunately, data are not available over a lower range of concentration owing to the marked slowing down of the reaction. Figs. 1 and 2 will be discussed further, later in the paper. Table II presents results of additional experiments in the more dilute sodium chloride solutions. Fresh solutions of the reactants were made up in practically the same concentration as before.

When Expts. 1 of Tables I and II are closely compared, it will be noted that different values for log k are obtained for solutions of the same ionic strength. This inconsistency was due to some undetermined source of error, perhaps caused by incorrect standardization of the sodium thiosulfate used in the second set of experiments. However, the error is a constant one and does not invalidate the conclusions drawn from the data. All of the runs in Table II were performed within a few days and it is improbable that any change occurred in the strength of the thiosulfate during that period.

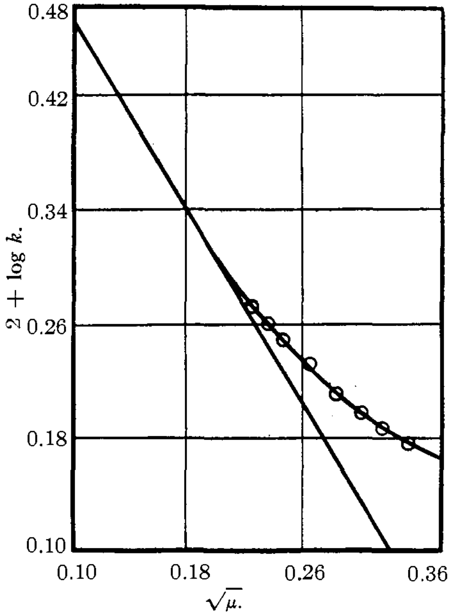

Fig. 2.—Showing the variation in the first-order constant with the sodium chloride concentration. The curve approaches a theoretical tangent of about -1.65.

Experiments at High Neutral Salt Concentration

In carrying out this series of experiments, the data from which are given in Table III, 1.5 M sodium chloride solution was used in each of the seven runs, the first four involving change of iodide concentration only and the last three change of acid concentration. The concentration of the dichromate was 2.02×10^{-4} *M* in all the runs. Table IV gives similar data for three runs in which no salt was added.

TABLE III

SHOWING VELOCITY OF REACTION WITH THE DICHROMATE CONCENTRATION LOW AND VARYING THE IODIDE AND ACID CONCENTRATIONS IN TURN. 1.5 *M* SODIUM CHLORIDE

Time, min.	0.00986 *M* $Na_2S_2O_3$, cc.	k
Run 8. Init. C_{KI}, 142 × 10^{-4} *M*. Init. C_{HClO_4}, 364.8 × 10^{-4} *M*. Av. $k/(H^+)^2(I^-)^2$, 8.20 × 10^4		
5	1.18	0.0202
10	2.22	.0197
15	3.19	.0203
20	3.96	.0177
30	5.40	.0190
45	6.98	.0174
75	9.29	.0190
120	10.98	.0184
Run 9. Init. C_{KI}, 71.0 × 10^{-4} *M*. Init. C_{HClO_4}, 364.8 × 10^{-4} *M*. Av. $k/(H^+)^2(I^-)^2$, 11.66 × 10^4		
5	0.44	0.0073
10	0.88	.0076
15	1.35	.0084
20	1.70	.0065
30	2.44	.0072
45	3.40	.0068
75	5.10	.0071
120	6.50	.0052
Run 11. Init. C_{KI}, 106.5 × 10^{-4} *M*. Init. C_{HClO_4}, 364.8 × 10^{-4} *M*. Av. $k/(H^+)^2(I^-)^2$, 9.76 × 10^4		
5	0.86	0.0145
10	1.58	.0130
15	2.30	.0139
20	3.02	.0150
30	4.10	.0124
45	5.42	.0117
75	7.38	.0112
120	9.38	.0116
Run 10. Init. C_{KI}, 284 × 10^{-4} *M*. Init. C_{HClO_4}, 364.8 × 10^{-4} *M*. Av. $k/(H^+)^2(I^-)^2$, 6.85 × 10^4		
5	3.36	0.0640
10	5.81	.0642
15	7.62	.0655
20	8.91	.0647
Run 12. Init. C_{KI}, 142 × 10^{-4} *M*. Init. C_{HClO_4}, 181.2 × 10^{-4} *M*. Av. $k/(H^+)^2(I^-)^2$, 10.30 × 10^4		
10	0.72	0.0068
15	1.08	.0063
20	1.45	.0067
33	2.20	.0055
45	2.93	.0063
75	4.46	.0060
Run 13. Init. C_{KI}, 142 × 10^{-4} *M*. Init. C_{HClO_4}, 273 × 10^{-4} *M*. Av. $k/(H^+)^2(I^-)^2$, 9.20 × 10^4		
5	0.80	0.0135
10	1.48	.0122
15	2.14	.0126
30	2.98	.0102
45	3.88	.0114
75	5.20	.0115
120	7.27	.0128
Run 14. Init. C_{KI}, 142 × 10^{-4} *M*. Init. C_{HClO_4}, 454.2 × 10^{-4} *M*. Av. $k/(H^+)^2(I^-)^2$, 8.09 × 10^4		
5	1.81	0.0319
10	3.27	.0300
20	5.68	.0269
30	7.39	.0299
57	9.98	.0279

As before, the values of *k* were calculated on the assumption that the velocity of the reaction was proportional solely to the concentration of the dichromate, owing to the fact that the concentration of the other two reactants was high in comparison to that of the dichromate. The assumption of fixed H^+ and I^- is not entirely justified, particularly in Runs 9 and

Table IV

Showing Velocity of Reaction with the Dichromate Concentration Low and Varying the Acid Concentration Only. No Neutral Salt Added

Run 1R. Init. I^-, 142 × 10^{-4} *M*. Init. H^+, 730 × 10^{-4} *M*. $Na_2S_2O_3$, 0.01032 *N*.
Av. $k/(H^+)^2(I^-)^2$, 11.78 × 10^4

Time in minutes	5	10	15	20
$Na_2S_2O_3$ used, cc.	4.70	7.42	9.32	10.34
k	0.1023	0.0976	0.1159	0.1095

Run 2R. Init. I^-, 142 × 10^{-4} *M*. Init. H^+, 547.6 × 10^{-4} *M*. $Na_2S_2O_3$, 0.01029 *N*.
Av. $k/(H^+)^2(I^-)^2$, 9.55 × 10^4

Time in minutes	6	10	15	20	30	45
$Na_2S_2O_3$ used, cc.	3.00	4.60	6.06	7.26	9.02	10.52
k	0.0490	0.0503	0.0455	0.0472	0.0495	0.0526

Run 3R. Init. I^-, 142 × 10^{-4} *M*. Init. H^+, 365.1 × 10^{-4} *M*. $Na_2S_2O_3$, 0.01007 *N*.
Av. $k/(H^+)^2(I^-)^2$, 8.24 × 10^4

Time in minutes	5	10	15	20	30	45
$Na_2S_2O_3$ used, cc.	1.14	2.18	3.02	3.86	5.38	7.20
k	0.0199	0.0201	0.0178	0.0196	0.0206	0.0213

12, as may be seen by comparing the concentrations in Table III. However, in evaluating the expression $k/(H^+)^2(I^-)^2$, used in Figs. 3, 4, 5 and 6, a correction was made to take into account the change in iodide and hydrogen-ion concentration during the course of a run. This was made by

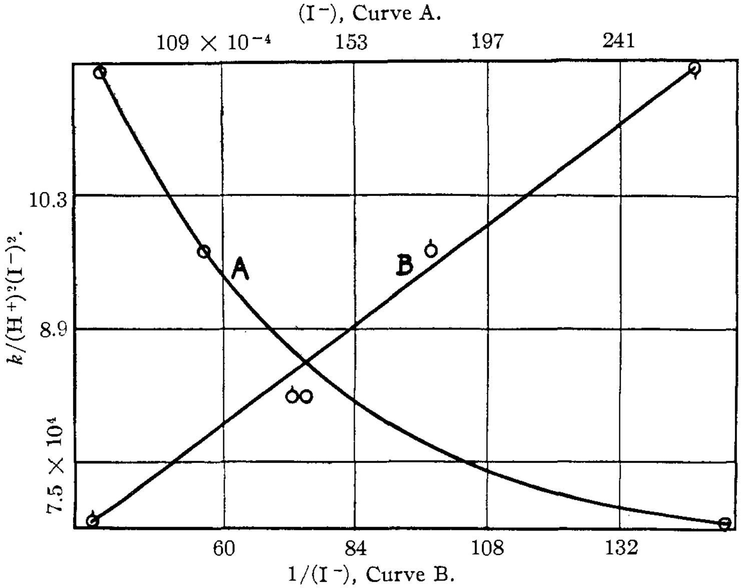

Fig. 3.—Curve A shows that the reaction is not second order with respect to (I^-). Curve B shows that the reaction consists of two simultaneous reactions, one involving (I^-) and the other $(I^-)^2$.

calculating the concentration of the iodide and acid left at the end of each time interval and dividing the product of the squares of these values into the corresponding value for k previously determined. The following example shows the method of calculation. In Run 10 the iodide used up in the first five minutes was equivalent to 3.36 cc. of 0.00986 N sodium thiosulfate. Consequently, $3.36 \times 0.00986 \times 10^{-3} = 3.31 \times 10^{-5}$ (the number of moles used up in 100 cc. of the reaction mixture), or 3.31×10^{-4} per 1000 cc. of the reaction mixture. The concentration of the iodide at the end of the first five minutes will then be equal to 284×10^{-4} minus 3.31×10^{-4} or 280.69×10^{-4} moles per liter. Multiplying 3.31×10^{-4} by 7/3

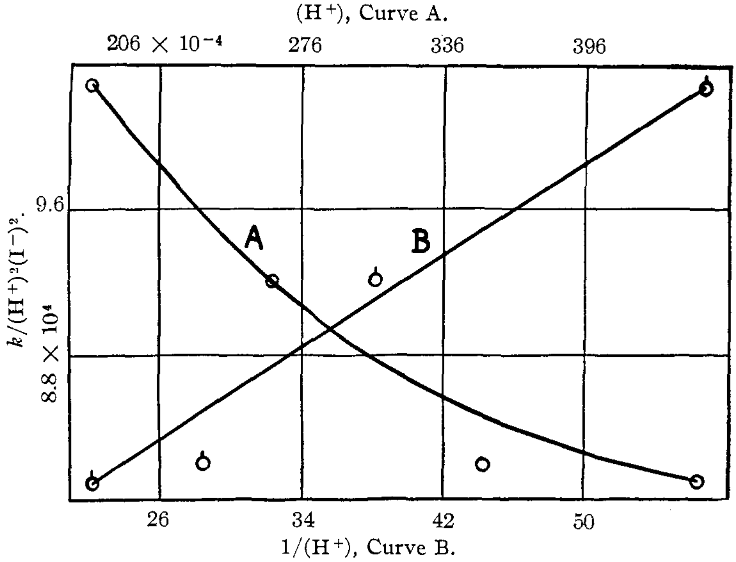

Fig. 4.—Curve A shows that the reaction is not second order with respect to (H^+). Curve B shows that the reaction consists of two simultaneous reactions, one involving (H^+) and the other $(H^+)^2$.

and subtracting from 364.8×10^{-4} will give the concentration of the acid at the end of the first five minutes, 357.07×10^{-4} moles per liter. The corresponding value of the velocity constant is seen to be 0.0640. Consequently $k/(H^+)^2(I^-)^2 = 0.0640/(280.69)^2(357.07)^2(10^{-3})^2 = 6.39 \times 10^4$.

While the usual method is to use the initial values of the concentration of those reactants which are in excess, we believe that this method of calculation is a more accurate treatment of the experimental results. In Table V is given the average value of $k/(H^+)^2(I^-)^2$ for each run, computed in this way, as well as the other data used in Figs. 3, 4, 5 and 6.

In Fig. 3 are shown plots of these values against the iodide concentration (Curve A) and against the reciprocal of the iodide concentration (Curve B) for Runs 8, 9, 10 and 11. Curve A, Fig. 3, shows that the reaction is not

Table V

Values Used in Figures 3, 4, 5 and 6

Run	Av. H^+ $\times 10^4$	Av. $1/H^+$	Av. I^- $\times 10^4$	Av. $1/I^-$	Av.$(1/H^+)\cdot(1/I^-) \times 10^{-3}$	Av. $k/(H^+)^2\cdot(I^-)^2 \times 10^{-4}$
1R	711.1	14.06	133.5	74.90	..	11.78
2R	531.4	18.82	135.1	74.02	..	9.55
3R	356.2	28.07	138.2	72.36	..	8.24
8	352.4	28.38	136.6	73.22	2.08	8.20
9	358.5	27.89	68.3	146.4	4.09	11.66
10	350.0	28.57	277.7	36.05	1.03	6.85
11	355.0	28.16	102.3	97.75	2.76	9.76
12	176.3	56.73	139.9	71.47	4.05	10.30
13	262.4	38.12	137.7	72.62	2.77	9.22
14	441.3	22.66	136.5	73.26	1.66	8.09

second order with respect to iodide concentration, because if this were so $k/(H^+)^2(I^-)^2$ would be constant from run to run and a straight horizontal line would be obtained in the plot. If two simultaneous reactions were going on here, one of which was first order and the other second order

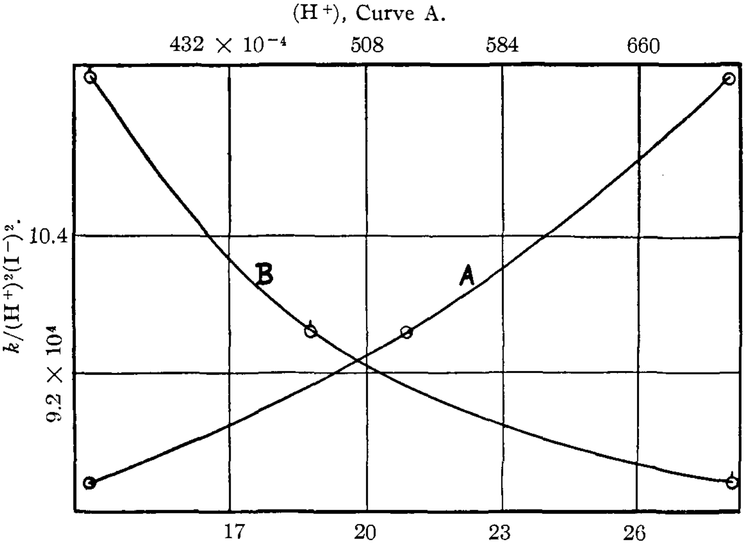

Fig. 5.—Showing that no simple interpretation of the data is possible in the absence of neutral salt. Straight line relations are not obtained.

with respect to I^-, the general expression for the velocity constant would be $k = k_1I^- + k_1k_2(I^-)^2$. Dividing through by $(H^+)^2 \times (I^-)^2$, this expression becomes $k/(H^+)^2(I^-)^2 = k_1/(H^+)^2(I^-) + k_1k_2/(H^+)^2$. Consequently, if $k/(H^+)^2(I^-)^2$ be plotted against $1/(I^-)$, a straight line should be obtained, since in the four series of experiments the concentration of acid was not varied. In Curve B, Fig. 3, the points fall approximately on a straight line.

The data for Runs 8, 12, 13 and 14 were treated similarly with results as shown in Fig. 4. Curve A shows that the reaction is not second order with respect to (H^+). Curve B indicates that the reaction is really composed of two simultaneous reactions, one of which is first order and the other second order with respect to (H^+).

Figure 5 shows the results of similar plots in the case of Runs 1R, 2R and 3R. Again Curve A is the plot of $k/(H^+)^2(I^-)^2$ against H^+, while curve B is the plot against $1/H^+$. Here it is seen that neither curve is capable of any simple interpretation. In this series of experiments no salt was present to fix the activity coefficients. Not only is Curve B not a straight line, but even the direction of B is reversed, the slope being negative instead of positive. The slope is also reversed in A. A comparison of Figs. 4 and 5 clearly indicates the beneficial effect of adding a neutral salt in making velocity studies of this type. It is important to note that the data in the absence of salt are incapable of any simple interpretation, as may be seen from Fig. 5, but when salt is added the difficulties of interpretation disappear as seen from the straight-line relation in Fig. 4.

Rate Constants for the Two Simultaneous Reactions

The discussion from this point bears entirely on the experimental results obtained in presence of 1.5 *M* NaCl. If the assumption is made that two simultaneous reactions occur, the observed velocity constant may be split into two factors, as follows

$$k = k_a(H^+)(I^-) + k_ak_b(H^+)^2(I^-)^2$$

where one reaction involves H^+ and I^- each to the first power and the other involves H^+ and I^- each to the second power. Dividing through by $(H^+)^2(I^-)^2$, we obtain the relation

$$k/(H^+)^2(I^-)^2 = k_a/(H^+)(I^-) + k_ak_b$$

where k_a is the velocity constant for the trimolecular reaction and k_ak_b the corresponding velocity constant for the pentamolecular reaction. In Fig. 6 the "5th order constant" $k/(H^+)^2(I^-)^2$ has been plotted as a function of $1/(H^+)(I^-)$. It follows from the equation just given that the slope of the best straight line through these points should be k_a. This has a value of 14.62. The pentamolecular constant has been evaluated from the data and found to be $k_ak_b = 53{,}000$. Taking these values as correct, one may calculate what the "observed velocity constant" should be to give exact agreement with this line. The data are recorded in Table VI. The calculated values of k were obtained from the straight line of Fig. 6 by picking off the values of $k/(H^+)^2(I^-)^2$ corresponding to the different values of $1/(H^+)(I^-)$ and solving for k.

Table VI

Velocity Constants in Runs Involving 1.5 M NaCl

Run	8	9	10	11	12	13	14	
Av. k, obs.	0.0189	0.0070	0.0646	0.0127	0.0063	0.0122	0.0293	
Av. k, calcd.	0.0195	0.0068	(0.0646)	0.0124	0.0068	0.0123	0.0283	
Deviation, %	3.0	3.0	0.0	2.0	7.0	1.0	3.5	Av., 3.0

The average percentage deviation of 3% is within the limit of error for the actually observed constants, k.

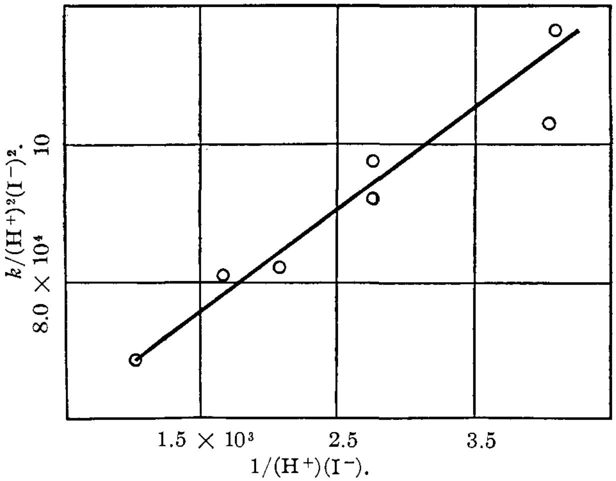

Fig. 6.—A combination of the two B curves in Figs. 3 and 4, showing that the reaction consists of two simultaneous reactions, one involving (H^+) and (I^-), the other $(H^+)^2$ and $(I^-)^2$.

Discussion of Figures 1 and 2

In the experiments recorded in Table II and Fig. 2, on the effect of varying sodium chloride concentration on the reaction velocity, the H^+ and I^- ion concentrations were 0.03643 and 0.0142 M, respectively. Substituting these values in the equation $k = 14.6(H^+)(I^-) + 53{,}000(H^+)^2(I^-)^2$, one obtains the following result, $k = 0.0076 + 0.0142$. Thus, μ being 1.55, the fraction $0.0142/(0.0142 + 0.0076) = 0.651$ (or about 65%) of the iodide is oxidized by the pentamolecular reaction.

As will be seen from an inspection of Fig. 1, the rate is practically the same in solutions of ionic strength ranging from $\sqrt{\mu} = 0.1$ to $\sqrt{\mu} = 0.2$ as it is in a 1.5 M sodium chloride where $\mu = 1.55$ or $\sqrt{\mu} = 1.25$. If hydriodic acid is like hydrochloric acid, the activity coefficient of hydriodic acid (*i. e.*, f_Hf_I) is also practically the same in these two solutions, namely, about 0.9. It is a consequence of the Brönsted theory that the ratio of the pentamolecular to the trimolecular rate will be proportional to f_Hf_I.[8]

[8] $h_5/h_3 = [(H^+)(I^-)k_5/k_3]f_{H^+}f_{I^-}$.

Consequently, about 65% of the oxidation should take place by the pentamolecular reaction *in the dilute solution.* The theoretical Brönsted slope should therefore be not -1 nor -2 but about -1.65, and is so drawn in Fig. 2. The lowest ionic strength investigated, $\sqrt{\mu} = 0.226$, is still too high for the simple Debye–Hückel equation to apply, but the trend of the experimental curve is such as to indicate -1.65 as being a reasonable value for the limiting slope in the most dilute solutions. It is therefore felt that Brönsted's treatment gives the correct interpretation of the experimental data in the less concentrated sodium chloride solutions. We do not wish to claim that -1.65 is the exact limiting slope, since $f_{\mathrm{H}} f_{\mathrm{I}}$ increases from about 0.9 to 1 as the ionic strength changes from $\sqrt{\mu} = 0.15$ to $\sqrt{\mu} = 0$, but merely to emphasize the point that on account of the two simultaneous reactions the limiting slope cannot be an integral number. However, the limiting slope cannot be far from -1.65.

Discussion of the Probable Chemical Changes

DeLury[3] has stated that his measurements indicate the possibility of two simultaneous reactions which affect the measured rate. Bray[9] has suggested that these may be

$$2\mathrm{I}^- + 2\mathrm{H}^+ + \mathrm{Cr_2O_7}^{--} = 2\mathrm{IO}^- + \mathrm{H_2Cr_2O_5} \qquad (1)$$

$$\mathrm{I}^- + 2\mathrm{H}^+ + \mathrm{Cr_2O_7}^{--} = \mathrm{IO}^- + 2\mathrm{HCrO_3} \qquad (2)$$

It is evident from the experimental results presented in this paper that Reaction 2 involving $2\mathrm{H}^+$ ions per I^- ion cannot be a slow reaction and affect the rate. If this were so the plot of $k/(\mathrm{H}^+)^2(\mathrm{I}^-)^2$ against H^+ in Fig. 4 would be a horizontal straight line or, in other words, the "5th order constant," $k/(\mathrm{H}^+)^2(\mathrm{I}^-)^2$ would be independent of the H^+ ion concentration. Fig. 4 shows a definite linear relation of $k/(\mathrm{H}^+)^2(\mathrm{I}^-)^2$ to $1/\mathrm{H}^+$.

The fact that a satisfactory representation of the experimental results in high neutral salt concentration is given by the equation

$$k = 14.6\ (\mathrm{H}^+)(\mathrm{I}^-) + 53{,}000\ (\mathrm{H}^+)^2(\mathrm{I}^-)^2$$

indicates that the two slow steps in the reaction are probably

$$\text{(I)}\quad \mathrm{H}^+ + \mathrm{I}^- + \mathrm{Cr_2O_7}^{--} \longrightarrow \ldots \text{ and}$$

$$\text{(II)}\quad 2\mathrm{H}^+ + 2\mathrm{I}^- + \mathrm{Cr_2O_7}^{--} \longrightarrow \ldots\ldots$$

Although the experimental evidence points clearly to the occurrence of a tri- and a pentamolecular reaction, it is not necessary to assume the simultaneous collision of more than two molecules. Starting with the Brönsted rate equations for only rapid reversible *bimolecular* reactions, one may readily combine them to obtain the correct kinetic equations for reactions of the third and fifth order, which satisfy the experimental data. The following equations were thus obtained

$$h_3 = k_3(\mathrm{H}^+)(\mathrm{I}^-)(\mathrm{Cr_2O_7}^{--}) \times f_{\mathrm{H}^+} f_{\mathrm{I}^-} \times f_{\mathrm{Cr_2O_7}^{--}}/f_{\mathrm{X_1}^{--}}$$

$$h_5 = k_5(\mathrm{H}^+)^2(\mathrm{I}^-)^2(\mathrm{Cr_2O_7}^{--}) \times f^2_{\mathrm{H}^+} \times f^2_{\mathrm{I}^-} \times f_{\mathrm{Cr_2O_7}^{--}}/f_{\mathrm{X_2}^{--}}$$

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[9] Bray, *Z. physik. Chem.*, **54**, 491 (1906).

Summary

Measurements have been made on the velocity of the stoichiometrical reaction $Cr_2O_7^{--} + 6I^- + 14H^+ = 2Cr^{+++} + 7H_2O + 3I_2$ at various concentrations of the reacting ions and in presence and absence of a neutral salt, sodium chloride. All experiments were carried out at 25°.

In dilute solutions the results offer confirmation of the Brönsted activity rate theory of reaction velocity.

In more concentrated solutions in the absence of a neutral salt, the kinetic behavior is incapable of any simple interpretation.

In the presence of 1.5 *M* sodium chloride as neutral salt, the kinetic anomalies disappear. The experimental results clearly indicate that two simultaneous reactions are taking place which may be represented as follows

$$H^+ + I^- + Cr_2O_7^{--} \longrightarrow HI\cdot Cr_2O_7^{--} \qquad (1)$$
$$2H^+ + 2I^- + Cr_2O_7^{--} \longrightarrow (HI)_2\cdot Cr_2O_7^{--} \qquad (2)$$

The observed velocity constant k is given to within an accuracy of 3% by the expression $k = 14.6\,(H^+)(I^-) + 53{,}000\,(H^+)^2(I^-)^2$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE RATE OF RECOMBINATION OF ATOMIC HYDROGEN

BY HUGH M. SMALLWOOD

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It has been pointed out by a number of investigators[1] that certain exothermic reactions of the type $A + B \longrightarrow AB$ cannot result from simple binary collisions of molecules A and B since, in such a collision, there is no means by which the energy corresponding to the heat of the reaction may be removed from the colliding molecules. In order to react the molecules must collide in the immediate neighborhood of some other object such as another molecule or the wall of the containing vessel. In other words, the reaction can only take place as the result of triplet impacts or three-body collisions.

A few limitations must be made to the foregoing statement. Thus, if there is a possibility of radiation occurring during the collision of molecules A and B, combination may result from a single collision since the energy of combination may be radiated from the system as light. Further, if molecules A and B are relatively complex, the energy of combination may be taken up by their internal degrees of freedom.

[1] Boltzmann, "Gastheorie. II," Leipzig, **1912**; Herzfeld, *Z. Physik*, **8**, 132 (1922); Born and Franck, *Ann. Physik*, **76**, 225 (1925); *Z. Physik*, **31**, 411 (1925); J. H. Jeans, "The Dynamical Theory of Gases," 4th ed., Cambridge University Press, p. 195.